STUDIES ON THE LIGHT ABSORPTION OF WATER-ALCOHOLIC SOLUTIONS IN THE NEAR INFRARED SPECTRUM RANGE

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(Received June 5, 1956)

In this paper the effect of alcohol, LiCl, CsCl and $Ni(ClO_4)_2$ on the light absorption of the water in the near infrared was studied.

1. On the basis of our examinations made on the series of alcohol-water it was found that the band at 1,2 μ may be attributed to mole-association, while at 0,99 μ is the overtone of some O-H ground vibration. Besides, the change of the absorbability of water is due to the influence of alcohol in consequence of the formation of alcohol-water collective associata. The formation of these associata reaches equilibrium at the alcohol-water ratio of 1 : 4 molecules, i. e., one mole alcohol associates with 3—4 moles of water in the collective associata.

2. Due to the influence of LiCl and CsCl, respectively the absorbability of water increased in the spectrum range at 1,30—0,99 μ stronger in the case of CsCl. On the basis of our interpretation of this fact it was supposed that the Li^+ and Cs^+ ions play a part similar to that of the nuclei in the formation of associata, so the increase of the associata causes the increase of the absorbability.

3. That the Ni^{++} ion has its own absorption of light in the range of 1,20—0,99 μ was shown by the examinations made with aqueous solutions of $Ni(ClO_4)_2$.

The electronic origin of the band appeared in this range, was stated, i. e., this band is not due to the overtone of the ground vibration of the hydrated ion.

Concerning the examinations of the solutions of $Ni(ClO_4)_2$, the slight effect of ClO_4 ions on the absorption of water in the near infrared was shown.

On the basis of the investigations by ILSE, HARTMANN and SCHLÄFER [1], [2] and KISS [3] the absorption bands — appearing in the visible range — of unoccupied d-orbital of hydrated metal ions and electrostatical complexes are caused by splitting of the *d* term into several terms or by intercombination. There appears as many bands as are the transitions possible among the split terms. The number of terms arising from the splitting of the ground term again depends on the potential-symmetry of the bound radicals, on the number of the unshared electrons and on the ground term.

The aim of this paper is to investigate in what wave length range the term-splitting band appears. Examinations were made regarding the absorption spectrum of Ni^{2+} ion in the range 0,9—1,3 μ.

Experimental

Metal salts LiCl and CsCl and $HClO_4$ »Merck p. a.« were used for solutions. $Ni(ClO_4)_2$, was prepared from cobalt free $NiCl_2$ »Merck p. a.« solving its carbonate in $HClO_4$ and crystallising it. Ethanol and tridistilled water were used as solvents. The concentrations of the solutions were given in mol/1000 g solution and the following equation for its calculation:

$$X = \frac{a \,.\, 1000}{(a+b) \,.\, M}$$

where a is the quantity of the material in question in grams, b means grams of the other component present i. e. of the solvent, M the molecular weight of the substance solved. The series of alcohol-water, LiCl-water and $Ni(ClO_4)_2$-water were prepared with dilution, the concentrations were given in weight concentration measuring the volume of the solution and calculated the weight concentrations on the basis of the determinations of the specific gravities. Both the weighing and the dilution were made by weight.

The spectra were determined by BECKMAN Model DU spectrophotometer using standard cells of 1,0 cm and reading at intervals of 10 $m\mu$.

Results and discussion

a) Series of alcohol water. Since water or mixture of alcohol and water are employed in general as solvents for inorganic salts i. e. complexes, it was the absorption bands of these solvents that were studied in the range of 0,9—1,3 μ (Fig. 1, curve 1). The bands were obtained for distilled water, as compared to air, at 1,2 and 0,99 μ in fair agreement with the examinations of COLLINS [4] and other authors [5], [6]. In MECKE's opinion [7], [8], [9] infrared spectrum of pure water may be attributed to valency and deformative vibrations. PLYLER [10] observed the ground vibration of ν_2 and ν_3 at 6,27 and 2,60 μ According to MECKE et al. [11], [12], [13] the other bands of water appeared in the visible and in the near infrared are the overtones of these ground vibrations. STANSFELD [14] demonstrated that, the temperature, especially of higher degrees, shifts the

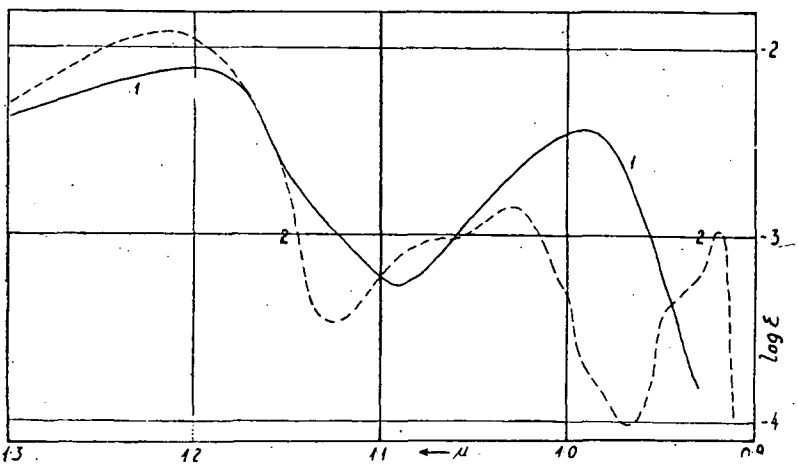

Fig. 1. Curve 1. : H_2O, Curve 2. : C_2H_5OH (measured with reference to air, calculated with the concentration of H_2O and C_2H_5OH, respectively).

bands to a slight extent in the range at 1,2—3,2 μ, making the molecular association responsible for it [15]. In COLLINS' opinion [4] a difference may be found between the spectrum of liquid water and that of its vapor in the bands at 0,97 and 1,2 μ owing to the presence of molecules of various kinds.

Absorption bands may be also found in the same range for ethylalcohol [16], [17], [18]. Our measurements are somewhat differing from those in the literature. The appearance of a new band has been observed at 0,92 μ with an inflection about 0,94 μ. A sharp band was noted at 1,03 μ, besides a weak one appeared at 1,08 μ. The above mentioned authors must have likely observed the overlapping of these two bands (Fig. 1, curve 2).

The band at 1,2 μ lies about there where these authors had observed it. The band appeared at 0,92 μ is missing for pure water, consequently may be attributed to the overtone of some of the C—H ground vibrations.

The spectra of alcohol-water mixtures at various proportions with reference to air and the validity of BEER's law have been examined. The log molecular extinction coefficient of both the alcohol and of water was calculated with D_{max} values obtained experimentally for the mixtures by the law of BEER and LAMBERT:

$$\log \varepsilon = \log D - \log c \quad ,$$

where c means the molarity of alcohol and of water, respectively, and D is the optical density $\log I_o/I$. The optical density of mixed solutions, at a given wave length, is composed of the optical densities of the components in pure state obtained at same wave length, unless the components affect each other.

$$D_{mixt.} = D_1 + D_2 \quad .$$

The molecular extinction values, $\log \varepsilon_a$ and $\log \varepsilon_w$ have been read for the spectra of pure alcohol and of pure water, respectively, at wave lengths where the mixed solutions had their maximum, wherefrom the optical densities are:

$$D_a = \varepsilon_a \cdot c_a \qquad \text{and} \qquad D_w = \varepsilon_w \cdot c_w,$$

where c_a and c_w mean the concentration of the alcohol and that of water, respectively, contained in the mixtures. So:

$$D_{mixt.} = \varepsilon_a \cdot c_a + \varepsilon_w \cdot c_w .$$

If the value of the D_{max} thus obtained is derived by the concentration of the alcohol or of the water contained in the mixture, the molecular extinction coefficient of the alcohol or of the water present in the mixture can be calculated on the basis of the spectrum of pure alcohol and that of pure water. Should the extinction values agree with those of the experiment, then the absorption of the mixture obeys BEER's law.

On the basis of the logarithms of the data thus obtained it could be stated with increasing concentration of the alcohol, as follows:

1. $\log \varepsilon_{a,\ max}$ of the band found about 1,20 μ considerably differs from the calculated one, this deviation being positive and decreasing when the concentration of the alcohol increases. However BEER's law appeared to hold true from about eight molecules and further increased alcoholic concentration.

2. At the same wave length the deviation of log $\varepsilon_{w,max}$ found is negative as compared to the calculated one and increases in the negative direction with increasing alcohol concentration. The deviation becomes positive and of a low value at about 8—12 molecular alcoholic concentration and, on increasing further the concentration, BEER's law appears to hold true.

3. The data of our calculations indicate that at the band of about 1,00μ BEER's law is valid for both the alcohol and water, except the first mixture where significant negative deviation was shown in both cases.

In the opinion of earlier authors these bands may be attributed to molecular association verified by COLLINS [19] on the basis of the influence of temperature of these bands. Thus they are caused by di- and trihidrol molecules, respectively. According to our calculations the absorbability of the alcohol-water mixture is greater, regarding the alcohol, and less, regarding the water, as compared to the computed one. In both cases the absorbability decreases with the concentration of the alcohol. This may be explained when the decrease of the concentration of the associata of alcohol and water, respectively, is assumed, as the collective associata of alcohol-water arise. At about a medium mole-ratio this process leads to equilibrium proved — in spite of the further increase of the alcoholic concentration — by the validity of BEER's law. No such deviations could be found for the band at about 1,00μ. This suggests that this band cannot be attributed to the mole-association, though a deviation was found between the observed and calculated values at a lower alcoholic concentration. At present no interpretation of this phenomenon can be given.

The afore-mentioned opinion is supported by Fig. 2, which contains the spectra of the series of alcohol-water mixture with reference to alcohol and calculating the log ε value with water concentration. For the reference cell contains

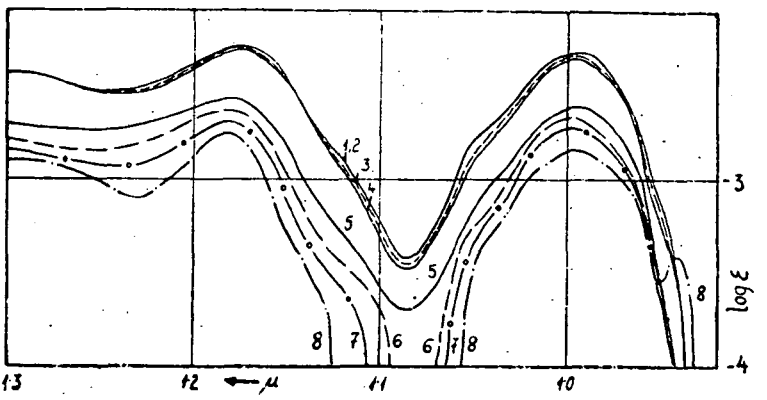

Fig. 2. Series of alcohol-water measured with reference to alcohol, calculated with the concentartion of H_2O

	Conc. of H_2O	Conc. of C_2H_5OH		Conc. of H_2O	Conc. of C_2H_5OH
1.	32,68 mol/l	8,92 mol/l	5.	23,98 mol/l	12,33 mol/l
2.	40,80 „	5,75 „	6.	16,55 „	15,23 „
3.	64,66 „	4,24 „	7.	13,23 „	16,53 „
4.	46,92 „	3,36 „	8.	11,35 „	17,77 „

the alcohol in higher concentration than the mixture, the absorption due to alcohol-alcohol associata is filtered. The split of the band into two bands (1,30 and 1,19 μ) at about 1,20 μ can be seen in Fig. 2 and because of the coincidence of the spectra BEER's law is valid up to medium alcoholic concentrations. For those alcoholic concentrations, whence — with reference to the air — the BEER's law became valid, however, gradually increasing deviations have been shown.

The interpretation of this phenomenon is as follows. The spectrum, with reference to the air, is due to three components: water-, alcohol- and alcohol-water associata. Using alcohol in the reference cell the alcohol associata are filtered and this is proved by the splitting of the band and by the decrease of the absorbability as compared to the absorption of pure alcohol or water and that of alcohol-water mixture determining the absorption with reference to air. In case of pure water the alcohol used for reference diminishes the height of the first band of the water due to absorption at the same spot. The alcohol added to the mixture draws a part of the molecules of the water to produce alcohol-water associata, thus the number of di- or trihidrol molecules are diminished. Consequently, the absorbability has to decrease with increasing alcoholic concentration. So the validity of BEER's law was found up to medium alcoholic concentration. An equilibrium of the formation of the alcohol-water associata was stated above at medium alcohol-water ratio. To attain this equilibrium, the concentration of the di- or trihidrol molecules decreases owing to the fact that molecules of water are drawn to produce alcohol-water associata followed by the decrease of absorbability. On the other hand, the concentration of the alcohol-water associata increases which presumably increases the absorbability too. Owing to the two contradictory effects the BEER's law is valid as long as the equilibrium is not attained. Having attained it, no more alcohol-water associata are produced, the concentration of the alcoholic molecules will simply diminish, decreasing simultaneously also the concentration of alcohol-water associata. Owing to the coöperation of these effects the extinction of the resulting curve will decrease. As the turning point is at about eight moles of the alcohol and thirty-two moles of the water, respectively, for both series, it may be supposed that the associatum is produced by one molecule of the alcohol and 3 to 4 molecules of the water. On the basis of these and owing to the shift of the curve toward the shorter wave lengths a greater interaction may be assumed between the molecules of alcohol and that of water than between the alcohol-molecules of the alcohol or the water-molecules of the water itself. Consequently the quasi crystalline structure of the water is disturbed not only by ions [20], but also by other liquids able to associate e. g. alcohols.

b) Series of LiCl and CsCl solutions. COLLINS [19] noted, as mentioned above, the spectra of the pure water and those of the solution will not coincide if the dissolved material has its effects on the absorption of water, or it has its own absorption. If the solution has less absorbability compared with that of the pure water, the dissolved material exerts its effect on the absorption of the water. On the basis of solvation theory this means the dissolved material produces a compound loosely bound with water whereby the solution absorbs less. On the other hand dehydrated materials have no effect on the absorption of the water, COLLINS, however, observed deviations from these statements, the inter-

pretation of which was given by LIVENS [21]. If the dissolved material possesses stronger absorption bands than the pure solvent, then the solvent absorbs less. Besides, earlier [22] it was found, that fixed water has a less absorbability than free one, and GANZ [23] established an agreement between the effect of the temperature and that of the dissolved salt on the basis of his examinations made on the solutions of colourless salts.

Bearing in mind the above mentioned facts the spectra of the solutions of LiCl. H_2O and those of CsCl were examined with reference to air in ten various dilutions and calculated the values of $\log \varepsilon_{max}$ with the concentrations of the water in every case at the bands of 1,02 and 0,99μ. At both bands the absorbability increased with increasing concentration of the salt reference to that of pure water. At the same time it was examined whether the ions mentioned above possess their own absorption on this range determining the absorptions of the solutions with reference to water.

In these cases, however, the absorption of light was not observed showing that the ions possess no absorption on this spectrum range. AZZAM [24] computed by means of statistical mechanics that the hydration number of Li^+ ion is six. The ion of Cs, however, does not hydrate shown on the basis of density measurements [20] and partial mole-volume [25], respectively. Moreover STEWART [26] has shown — examining the alcoholic solution of LiCl — the participation of both Li^+ and Cl^- ions with the molecules of solvents in the development of the cibotactic structure of the liquid. GANZ [23] studying the influence of dissolved salts pointed out the slight effect of Cl^- ions exerted on the absorption of water. It is known, however, that the complex-formation starts at higher concentration, which, in GANZ's opinion, would decrease the effect exerted on the absorption of water.

Considering the afore-said statements $LiCl.H_2O$ would exert an effect on the molecules of water. In spite of this effect the absorbability of the solution increased. The same was shown in the case of CsCl, though to a greater degree. It was repeatedly verified that the band at 1,2μ may be attributed to molecule-association. Accordingly, the increase of the absorption means the increase of the number of associated molecules. Taken into consideration STEWART's statements, Li^+ and Cl^- ions may be supposed to play such a role as the nuclei in forming the associata with the molecules of the solvent involving the increase of the concentration of the associated molecules and consequently that of the absorbability. The absorption was found greater in the case of the solution of CsCl than in that of LiCl. Its possible reason is that Cs^+ ions do not hydrate, thus there is no binding of water molecules. So it may be interpreted the apparent contradiction that the mentioned ions, though they do not possess their own absorption, still increase the absorption related to water.

c) Series of $Ni(ClO_4)_2$ solutions. Coloured metal ions possess definite absorption in the visible range attributed to the electrons of 3d-orbital [28], [29], [30]. The question arises, whether the bands in the near infrared are of electronic origin. DREISCH and KALLSCHEUER [31] studying various Cu, Ni and Co salts found qualitatively and quantitatively the same absorption in the near infrared shown by the salts of the same cation with various anions except the cupric acetate. The studies were extended also on the solutions of other coloured metal salts

with similar results [5]. Besides it was stated that the spectra of all the solutions of salts examined showed more or less a fine structure and the absorption bands of the same cation but with various anions differ from each other only in the fine structure, which can be explained by the appearance or arising of the effect of hydrated ions. Studying the infrared spectra of Co-amine complexes [32] vibrational bands in the far infrared were found, the overtones of which may spread to the near infrared. On the other hand, definite electronic bands were found in the near infrared investigating uranium and plutonium salts [33].

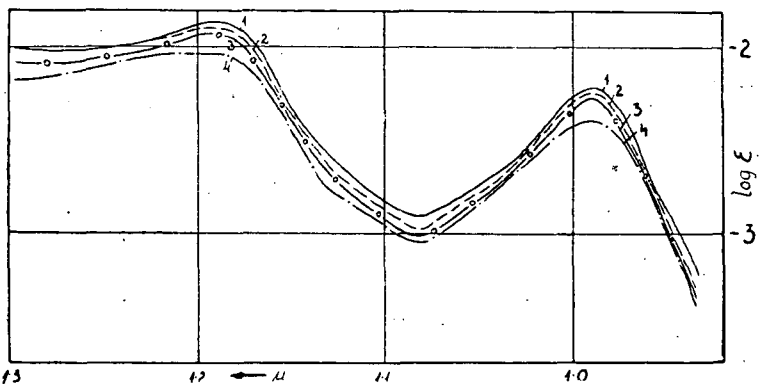

Fig. 3. Series of $HClO_4$ measured with reference to air, calculated with concentration of H_2O

	Conc. of $HClO_4$		Conc. of $HClO_4$	
1.	5,128	mol/l	3. 3,369	mol/l
2.	4,542	„	4. 0,761	„

For further examinations $Ni(ClO_4)_2$ was used as the Cl^- ions may have an effect on the absorption of water and owing to the slight complex-forming ability of the ClO_4^- ions [3], [35], [36]. In a series of examinations the effect of $HClO_4$ on the absorption bands of water has been studied (Fig. 3). In JÖRGENSEN's statement [6] the $HClO_4$ exerts only a third of the effect of the HNO_3. Our examinations, extended to the near infrared, stated the appearence of a new band at about 1,3 μ and the slight shift of the band at about 1,2μ to the shorter wave lengths. The increasing concentration of the $HClO_4$ increased the absorption. These effects may be assumed to be due to the formation of H_3O^+ ions. Namely, LECOMTE [37] observed the appearance of new bands at about 5,4 and 2,4μ attributed to hydrate bond of H_2O—HCl and H_3O^+ ions respectively. Owing to the appearance of a new band also at about 1,3μ for the series of alcohol-water with reference to alcohol, the close agreement between the vibrational energy of the hydrate bond of H_2O—$HClO_4$ and that of the alcohol-water associatum may be assumed. The effects themselves are not too strong, thus the effect of ClO_4^- anions has to be slight for metal perchlorates.

In the serial measurements with the solution of $Ni(ClO_4)_2$ of various concentrations with reference to air and computing the extinction with the concentration of water, the gradual appearance of the two well-known absorption bands of water was observed when decreasing the concentration of Ni^{++} ion (Fig. 4, a. series). On the other hand determining the spectrum with reference

to solvent and computing the extinction with the concentration of Ni^{++} ion a twin band was observed at about 1,12 μ which more or less obeys the BEER's law (Fig. 4 b. series). The extinctions of spectrum series were calculated:

$$\frac{\varepsilon_{Ni} \cdot c_{Ni} + \varepsilon_W \cdot c_W}{c_W}$$

where ε_{Ni} means the molar extinction coefficient of $Ni(ClO_4)_2$ (on the basis of the data of Fig. 4 b.), ε_W is the molar extinction coefficient of water (on the basis of Fig. 1), c_{Ni} and c_W mean the concentrations of $Ni(ClO_4)_2$ and water, respectively. The deviations between the observed and calculated extinctions are positive and taking the fluctuations as experimental error, constant. Owing to the positive deviation the $Ni(ClO_4)_2$, apart from its own absorption, in-

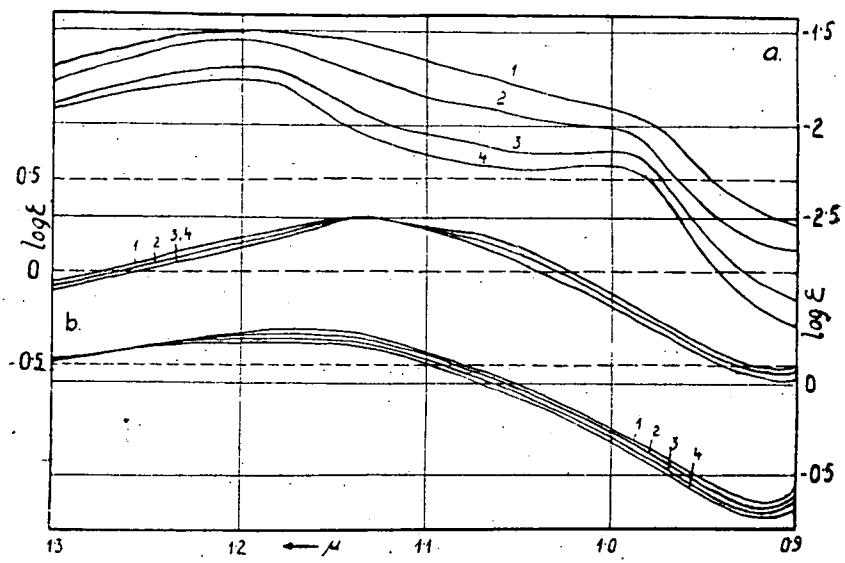

Fig. 4. a: Series of $Ni(ClO_4)_2$ measured with reference to air, calculated with the concentration of H_2O (concentration values in Table 5.; values of log ε on the right).

b: Series of $Ni(ClO_4)_2$ measured with reference to H_2O, calculated with the concentration of $Ni(ClO_4)_2$ (values of log ε on the left).

	Conc. of $Ni(ClO_4)_2$			Conc. of $Ni(ClO_4)_2$	
1.	1,011	mol/l	3.	0,569	mol/l
2.	0,763	„	4.	0,419	„

c: Series of $Ni(ClO_4)_2$ in the mixture of alcohol-water measured with reference to the same mixtures of solvents, calculated with the concentration of $Ni(ClO_4)_2$ (values of log ε on right).

	Conc. of $Ni(ClO_4)_2$		Conc. of C_2H_5OH		Conc. of H_2O	
1.	0,078	mol/l	3,565	mol/l	46,156	mol/l
2.	0,088	„	7,665	„	35,904	„
3.	0,092	„	14,432	„	18,602	„
4.	0,099	„	20,002	„	4,357	„

creased the absorbability of the water related to pure water. Thus it was assumed that the own absorption of Ni^{++} ion present dominates in the solution. This was verified by the series of measurements followed. Making several mixtures of nearly identical concentrations of $Ni(ClO_4)_2$ but with various alcohol-water ratio the spectra were determined with reference to the mixture of the same alcohol-water ratio (Fig. 4 c. series). The curves of the spectra have the same slopes thus supporting their electronic origin. Should this band be attributed to the ground vibration or to the overtone of any ground vibration, the various mixing ratios of the solvent mixture would have an effect on the vibrational state of the solvated Ni^{++} ion which would result a change in the spectrum.

The spectra of the same series were determined in the range of 700 mμ with reference to alcohol-water mixture but finding the band of each solution at the same place proves that the cause of the appearance of this band in the visible range is identical with that of the band in the near infrared. The correctness of our assumption is proved also by BALLHAUSEN's recently published quantummechanical calculations [38].

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The authors wish to express their appreciation to Prof. Á. KISS for his interest and helpful advice in the course of their work.

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